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14. ABSTRACT

Kapton® is used extensively in spacecraft thermal blankets, solar arrays, and space inflatable structures. This material is chosen due to its thermal and physical properties, however it is degraded severely in low Earth orbit (LEO) by atomic oxygen (AO). SiO_2 coatings impart remarkable oxidation resistance to Kapton®, yet imperfections in the SiO_2 application process and micrometeoroid debris impact in orbit may damage the SiO_2 coating and lead to Kapton® erosion. Polyhedral oligomeric silsesquioxane (POSS) is a silicon and oxygen cage-like structure surrounded by organic groups. POSS-diamine and the monomers of Kapton® were polymerized and cured to form POSS-polyimide (POSS-PI) films. These POSS-copolymers are self-passivating by the formation of a silica layer upon exposure to AO. Evidence of a SiO_2 passivation layer has been shown by X-ray photoelectron spectroscopy studies on AO exposed 3.5, 7.0, and 8.75 weight % Si_8O_{11} main chain (MC)-POSS-PI samples with erosion yields of 3.7, 0.98, and 0.3 percent, respectively, of the erosion yield for Kapton H® at a fluence of 8.5×10^{20} O atoms cm^{-2}. The self-passivation of POSS-PIs has also been demonstrated by monitoring a 1 micron deep scratch in AO-exposed main-chain-POSS-PI (MC-POSS-PI) after a second exposure to AO. A study of the effect of temperature on the AO erosion of POSS-PI samples showed that although the erosion of MC-POSS-PIs increased with temperature, they erode significantly less than their no-POSS analogues at elevated temperatures. POSS-polyimides flown for 3.9 years in low Earth orbit on the Materials International Space Station Experiment (MISSE) showed dramatically increased survival relative to 0 % POSS-polyimide. These results and physical property characterization of POSS-PIs exposed to AO, evidence that POSS-PIs are a viable Kapton® replacement material.

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SYNTHESIS AND CHARACTERIZAITON OF SPACE-SURVIVABLE POSS-KAPTON®-POLYIMIDES
(Preprint)

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ABSTRACT

Kapton® is used extensively in spacecraft thermal blankets, solar arrays, and space inflatable structures. This material is chosen due to its thermal and physical properties, however it is degraded severely in low Earth orbit (LEO) by atomic oxygen (AO). SiO_2 coatings impart remarkable oxidation resistance to Kapton®, yet imperfections in the SiO_2 application process and micrometeoroid debris impact in orbit may damage the SiO_2 coating and lead to Kapton® erosion. Polyhedral oligomeric silsesquioxane (POSS) is a silicon and oxygen cage-like structure surrounded by organic groups. POSS-diamine and the monomers of Kapton® were polymerized and cured to form POSS-polyimide (POSS-PI) films. These POSS-copolymers are self-passivating by the formation of a silica layer upon exposure to AO. Evidence of a SiO_2 passivation layer has been shown by X-ray photoelectron spectroscopy studies on AO exposed 3.5, 7.0, and 8.75 weight % Si_8O_{11} main chain (MC)-POSS-PI samples with erosion yields of 3.7, 0.98, and 0.3 percent, respectively, of the erosion yield for Kapton H® at a fluence of 8.5 x 10^{20} O atoms cm^{-2}.

The self-passivation of POSS-PIs has also been demonstrated by monitoring a 1 micron deep scratch in AO-exposed main-chain-POSS-PI (MC-POSS-PI) after a second exposure to AO. A study of the effect of temperature on the AO erosion of POSS-PI samples showed that although the erosion of MC-POSS-PIs increased with temperature, they erode significantly less than their no-POSS analogues at elevated temperatures.

POSS-polyimides flown for 3.9 years in low Earth orbit on the Materials International Space Station Experiment (MISSE) showed dramatically increased survival relative to 0 % POSS-polyimide. These results and physical property characterization of POSS-PIs exposed to AO, evidence that POSS-PIs are a viable Kapton® replacement material.

KEY WORDS: Space/Spacecraft/Satellite, Atomic Oxygen/Space Environmental Effects, Polyimide (PI).

1. INTRODUCTION

Kapton® polyimide is used extensively on spacecraft as a flexible substrate for lightweight, high-power solar arrays because of its inherent strength, temperature stability, excellent insulation properties, UV stability, and IR transparency. It is also used in conjunction with Teflon FEP in multilayer insulation blankets for thermal control insulation because of its superior optical properties, including low solar absorptance. In these multilayer insulation blankets, aluminium (or gold) is typically applied to Kapton® due to its low emissivity.[1]

It has been well established through space flight experiments in low Earth orbit (LEO) and ground-based simulations of atomic oxygen (AO) effects on LEO, that polymeric materials undergo severe degradation as a result of this aggressive environment encountered in LEO.[2-10] In this high vacuum, yet harsh environment, materials are subjected to solar radiation, thermal cycling which can range from -50 ˚C to 150 ˚C, bombardment by low and high-energy charged particles, and high fluxes of AO.[11] These harsh conditions necessitate the design of space-survivable materials.

AO strikes the ram surfaces of spacecraft in LEO with high relative velocities, corresponding to O atoms with a nominal translational energy of 4.5 eV incident on these surfaces. The ~1000 K temperature of the ambient atmosphere imparts a distribution of relative velocities to the collisions.[12-14] The high collision energies associated with the O-atom-surface collisions are sufficient to overcome many reaction barriers, thus enhancing the reaction probability and facilitating the degradation of Kapton® and other materials   Kapton® is has commonly been coated with silica to improve its resistance to AO. Imperfections in the silica layer created during the deposition process, handling, deployment, or flight lead to regions of unprotected Kapton®, which erodes readily in the presence of AO. It has been shown by de Groh et al. that when protective aluminim coatings are damaged in LEO, AO erosion can lead to spaces in the polymer matrix. AO can ricochet in the spaces before reacting, thereby burrowing out cavities, causing increased material erosion.[2]

The nanodispersion of Si and O throughout the polyimide polymer matrix leads to the formation of a protective silica layer on the polyimide surface when the material reacts with AO. Our data indicate that upon AO exposure of POSS-PI films, the surface organic material erodes, while atomic oxygen reacts with the nanodispersed POSS to form a silica passivation layer. Therefore, when POSS is copolymerized to form POSS-PI, it imparts remarkable AO resistance and does so with minor effects in the storage modulus, glass transition temperature, and coefficient of thermal expansion.[15]

Evidence for the formation of a protective silica layer on the surface of POSS-PIs upon exposure to AO was found in X-ray photoelectron spectroscopy (XPS) studies of POSS-PIs flown on MISSE1, and in separate studies of POSS-PIs exposed to AO in a ground-based facility. To directly compare the effect of AO on Kapton H®, SiO_2 coated Kapton HN®, and 8.75 weight % Si_8O_{11} cage "main-chain" POSS-polyimide (8.75 wt % Si_8O_{11} MC-POSS-PI), these materials were exposed to AO, scratched, and exposed to a second equivalent AO fluence. The erosion of the three materials, inside and outside of the scratched area, was monitored by stylus surface profilometry. The results of this study indicate that a silica layer is formed upon exposure of POSS-PIs to AO, and after scratching this layer, a new silica layer forms in the scratched area during AO exposure. Physical property characterizations of POSS-PIs, and the effects of a 3.9 year flight experiment involving POSS-PIs on the International Space Station are presented in this paper.

2. EXPERIMENTAL

2.1 Synthesis of POSS-Polyimide Copolymers Polyimides with the same chemical formula as Kapton® were synthesized by condensation polymerization of 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in an N,N′-dimethylacetamide (DMAc) solvent [15, 16]. A POSS dianiline monomer (Figure 1) with two 1-(4-aminophenyl)-pendant groups and eight cyclopentyl pendant groups was synthesized using a procedure described by Feher et al. in 2003 [17-22]. Using this monomer, POSS-polyimide random copolymers were synthesized as shown in Figure 1 with POSS monomer loadings corresponding to 0, 5, 10, 20, and 25 wt%, which correspond to Si_8O_{11} cage loadings of 0, 1.75, 3.5, 7.0, and 8.75 wt %. [18] "Side-chain"-POSS (SC-POSS) monomer was synthesized by Wright, et al. [19] from which 3.5, 7.0 wt % Si_8O_{12} cage SC-POSS-PIs were synthesized in the same manner as described above. All poly(amic acids) were cured to POSS-PIs as previously reported. [18]

2.2 Exposure of POSS-Polyimides to Low Earth Orbit POSS-PIs containing 0, 1.75, and 3.5 wt % Si_8O_{11}, were flown in LEO on the International Space Station as part of the Materials International Space Station Experiment 1 (MISSE-1). The samples were flown

in Passive Experiment Container 1 (PEC 1), in Tray 1, developed by NASA Langley Research Center (LaRC). The samples were assigned numbers 38, 39, 40. Prior to flight, the samples were set on aluminum disc substrates, set into the sample tray, and held into place by a top plate with open circles to expose the samples. The top plate also served as a mask for the outer ring of the samples because it protected this outer area from exposure to the space environment.

The flight was launched on August 10, 2001 and was retrieved after 3.9 years in LEO. Experiment details and images are available at http://misse1.larc.nasa.gov/. The circular samples were exposed to all aspects of the LEO environment including AO and UV light. The step height difference between this masked outer ring and the neighboring exposed sample area was measured in twelve places by profilometry. The surface atomic composition of the samples was determined by XPS.

2.3 AO Exposure of POSS-Polyimides Ground-based exposures of POSS-PI samples to AO were performed with a pulsed AO beam, operating at a repetition rate of 2 Hz and containing hyperthermal O-atoms that were generated with the use of a laser detonation source. [9, 23] The hyperthermal beam contains neutral O-atoms and molecular oxygen, with an ionic component of 0.01%. The mole fraction of AO in the beam was above 70 % and, for some exposures, above 90 %. The average kinetic energy of the O atoms in the beam is about 5.2 eV, with an energy width (full width at half maximum) of $\sim$ 2 eV. Prior to exposure, samples were covered with a stainless steel mesh disk in order to mask areas and achieve AO exposed and unexposed areas. The O-atom fluence was on the order of 10^{20} O-atoms cm^{-2} for all experiments. All samples in this work were handled in ambient air after exposure and prior to etch depth determination by profilometry, surface topography, and surface chemistry measurements. [24]
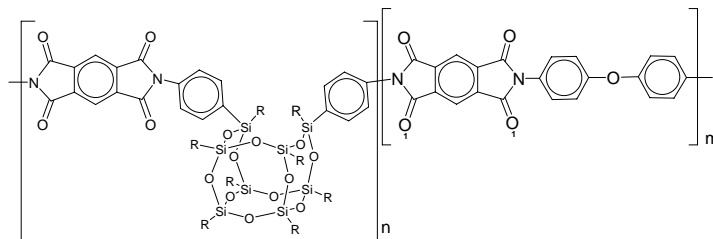

Figure 1. The structure of MC-POSS-Polyimide. R = cyclopentyl.

2.3.1 Surface Characterization of Scratched POSS-Polyimides Multiple samples of Kapton[®] H, 8.75 % Si_8O_{11} MC-POSS PI, and silica-coated Kapton HN[®] (provided by Astral Technology Unlimited, Inc. Lot No. 00625-007, with a 130 nm SiO_2 coating) were exposed to hyperthermal AO. The beam was produced by the laser detonation source previously described. [9,23] Three samples of each type were exposed to 100k

pulses of the beam, along with a Kapton H[®] standard. After the first exposure, the etch depths of the screened samples were measured. A set of unscreened samples underwent surface morphology measurements. The third set of samples was scratched. For each sample, one approximately 40 μm wide and 1μm deep was made with a diamond-tipped scribe, and two scratches approximately 20 μm wide and 1μm deep were made with a razor blade. All scratches were measured by profilometry (with a 5μm radius probe tip) in several places. Screens were placed over the scratched samples and these samples were exposed to an additional 100k shots of the hyperthermal AO beam. Each 100k-shot exposure corresponded to an O-atom fluence of approximately 2×10^{20} atoms cm^{-2}. After removal of the samples from the chamber, profilometry was used to measure step height differences between exposed and unexposed areas and to profile each scratch in AO exposed and unexposed areas.

XPS data was obtained with the use of non-monochromatized Mg Kα radiation (1253.6 eV) and a hemispherical CLAM 2 (VG Microtech) analyzer. Scanning electron microscopy (SEM) was performed using an ISI CL6 operating at 15 keV equipped with a Kevex X-ray detector, as previously reported. [18] Images of MISSE-flown samples were taken using a Leica MZ125 crystallography microscope.

2.3.2 The Effect of Temperature on Erosion of POSS-Polyimides by a Hyperthermal O-Atom Beam The erosion of 0 wt %, 3.5 wt % and 7.0 wt % Si_8O_{11} POSS-polyimides exposed to a hyperthermal O-atom beam has been studied at 25 ºC, 100 ºC, 150 ºC, 220 ºC, and 300 ºC. Two samples of each type of material were exposed simultaneously. One of each sample type was covered with a screen during exposure. Each exposure was to 50,000 pulses of the hyperthermal O-atom beam, and included a "screened" Kapton H[®] reference sample held at 23 ºC. The O-atom fluence was on the order of 10^{20} O-atoms cm^{-2}. The nominal O-atom translational energy of each exposure was 5.2 eV, and the O/O$_2$ ratio in the beam was 0.65:0.35. For the 25 ºC exposure, the films (which were not cast on substrates) were placed in the sample holder. For the higher temperature exposures, the films were cast on germanium discs that were in contact with a controlled heating block during the exposures, and were equilibrated to the desired temperature.

2.4 Physical Properties Characterization of POSS-Polyimides. Polyimide samples were analyzed by a DMTA V from TA Instruments using a 5 ºC/min temperature ramp from room temperature to 500 ºC and a tensile geometry.[18]

Measurements of the coefficient of thermal expansion (CTE) were taken on a thermo mechanical analyzer (TMA 2940) from TA Instruments with a film fiber attachment, in a nitrogen atmosphere. The cured films were cut into 15 mm by 3 mm samples, the force applied was 0.05 N & 0.10 N, and the sample was heated at 5 °C/min. The CTE was

calculated as $\alpha = (\Delta L \times K)/(L \times \Delta T)$ where L = length, K = a cell constant, T = temperature in °C. Test variability was +/- 2.306 ppm/ °C based on five Kapton H[®] tests.

3. RESULTS AND DISCUSSION

Most of the knowledge of the properties of POSS-PIs has been gained by their exposure to a ground-based simulated LEO environment. The AO exposure of 0, 3.5, 7.0, 8.75 wt % Si_8O_{11} MC-POSS-PI (POSS "R" group is cyclopentyl) films was carried out in a simulated LEO environment where films of these materials were etched by exposure to a hyperthermal O-atom beam. The difference in etch depth between the eroded and stainless steel screen-protected areas of the samples, made it possible to calculate an AO reaction efficiency (R_e) or erosion yield of the material for a given AO flux.[29]

The AO reaction efficiency of the Kapton H[®] reference sample was used to calculate the Kapton[®] equivalent fluence and erosion yields of each sample exposure.[29] For various exposures, the step heights (or etch depths) of POSS-PI films were plotted as a function of the step height of the Kapton H[®] film.[23] The derivative functions indicated that the 3.5 and 7.0 wt % Si_8O_{11} POSS polyimide films reached erosions rates of 3.7 and 0.98%, respectively, of the erosion rate for Kapton H[®] after 395,000 beam pulses (8.47 x 10^{20} atoms cm^{-2}).[9, 10] 8.75 wt% Si_8O_{11} MC-POSS-PI samples had an erosion rate that was 0.3 percent of the erosion rate for Kapton H[®], and 1/3 of 7.0 wt % POSS-PI at a fluence of 8.5×10^{20} atoms cm^{-2}. These results support the formation of a passivating silica layer that is a result of the reaction of AO with nano-dispersed POSS.

A "self-passivation test" was carried out to better assess the protective silica layer formation witnessed by XPS of POSS-PIs. Kapton H[®], SiO_2 coated Kapton HN[®], and 8.75 wt % Si_8O_{11} MC-POSS-PI were exposed to equivalent AO fluences. The etch depth of the Kapton H[®] after the initial exposure was 7.0 ± 0.2 µm, indicating an O-atom fluence of 2.3 x 10^{20} O atoms cm^{-2}. This sample appeared significantly roughened after exposure. The etch depth of 0.26 ± 0.15 µm of the 8.75 wt % Si_8O_{11} MC-POSS-PI film was difficult to measure since the overall etch depth was not much greater than the slight roughness caused by the exposure. For the SiO_2 coated Kapton HN[®] the etch depth was below the practical measurement limit of the profilometer and the sample surface appeared to be unaffected.

After the initial AO-exposure, Kapton H[®], SiO_2-coated Kapton HN[®], and 8.75 wt % Si_8O_{11} MC-POSS-PI were scratched and underwent a second exposure to 2.3 x 10^{20} O atoms cm^{-2}. SEM images of the results are shown in Figure 2. For the SEM image of Kapton H[®], the exposed region is in the left side of the image and has a more roughened surface with a deepened scratched area. The etch depth of the Kapton H[®] sample outside of the scratch was about 5.5 µm. The unexposed scratch was 20 µm wide and 1µm deep,

and increased in depth to 1.4 µm after the second exposure. The top of the SiO_2-coated Kapton HN$^{®}$ image was exposed to AO and only had erosion in the scratched area with unaffected neighboring silica-coated Kapton HN$^{®}$, demonstrating the effects of damage to silica coatings on Kapton$^{®}$. Here the unexposed scratch was 20 µm wide and 1µm deep and the exposed scratch was 8 µm deep relative to the neighboring exposed surface, amounting to 7 µm of erosion in the scratch. 8.75 wt % Si_8O_{11} MC-POSS-PI was exposed to AO in the darkened upper right area in Figure 2c. A difference in step height between exposed and unexposed unscratched areas of the 8.75 wt % Si_8O_{11} MC-POSS-PI was < 200 nm and is not visible by optical microscopy. In Figure 2c, the scratch was 35 µm wide and 1.4 µm deep unexposed and about 1.8 µm deep after AO exposure. This result indicates that 8.75 wt % Si_8O_{11} MC-POSS-PI experienced about 400 nm of erosion inside the scratch during AO exposure. In comparison, Kapton H$^{®}$ eroded about 5 µm inside and outside the scratch, plus Kapton H$^{®}$ eroded an additional 0.200 µm in the scratch during exposure. In all instances, the scratched regions apparently eroded slightly more than the unscratched exposed areas. This may be explained by the undercutting effect described above where the O-atoms are focused deeper into the polymer matrix by scattering from the sidewalls of the scratches. These results are summarized in Table 1.
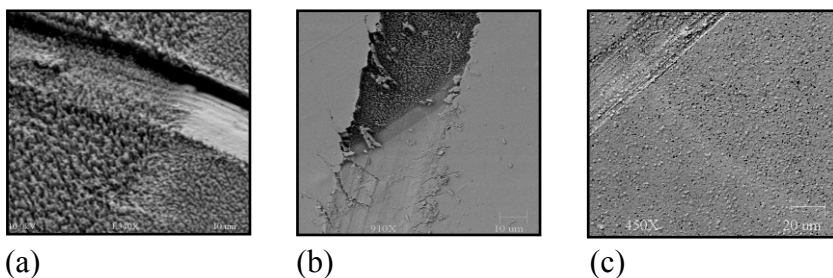

(a)   (b)   (c)

Figure 2. SEM images of results from a self-passivation experiment. (a) Kapton H$^{®}$, (b) SiO_2 coated Kapton HN$^{®}$ (Provided by Astral Industries Inc.), and (c) 8.75 wt % Si_8O_{11} cage MC-POSS-PI. Samples were exposed to 2.3 x 10^{20} atoms/cm^{2}, scratched, covered by a wire screen and exposed again to 2.3 x 10^{20} atoms cm^{-2}. The area covered by the wire screen was (a) the right side, (b) the bottom portion, and (c) the left side.

Table 1. Self-Passivation Experiment Erosion Depths

Material	Kapton H$^{®}$	SiO_2-coated Kapton HN$^{®}$ with Aluminum under-coating	8.75 wt % Si_8O_{11} MC-POSS PI
After 1st exposure.	5.5 µm	~ 0 µm	~ 0.200 µm
After 2nd exposure. Outside of scratch.	5 µm	~ 0 µm	~ 0 µm
After 2nd exposure. Inside of scratch.	5 µm	7 µm	~ 0.200 µm

The results of the study of the effect of temperature on AO erosion of POSS-polyimides are given in Tables 2 and 3 below. The results in Table 1 show that polyimide and POSS-PIs experience increasing erosion with increasing temperature. For each temperature, the etch-depths of the POSS-PIs (Table 2) divided by the etch depth of Kapton H$^®$ are given in Table 3. The erosion of the 0 wt % POSS-PI exhibited the strongest temperature dependence, with the etch depth increasing by a factor of about 3.6 from 25 ºC to 300 ºC. The 3.5 wt % and 7.0 wt % Si_8O_{11} POSS-PIs showed less temperature dependence in their erosion. The etch depths of these samples increase by factors of 2.2 and 2.4, respectively, with the increase from 25 ºC to 300 ºC. Taking into account the uncertainty in the measurements, these factors may be considered to be the same.

Table 2. The etch depths for polyimide, 3.5 wt % and 7.0 wt % Si_8O_{11} POSS-polyimides, and Kapton H$^®$ after exposure to a hyperthermal O-atom beam at five temperatures.

Temperature of the Sample	Polyimide (µm)	3.5 wt % Si_8O_{11} POSS-polyimide (µm)	7.0 wt % Si_8O_{11} POSS-polyimide (µm)	Kapton H$^®$ 23 ºC (µm)
300 ºC	10.37 ± 0.47	1.24 ± 0.17	0.67 ± 0.16	3.14 ± 0.13
220 ºC	7.47 ± 0.37	0.94 ± 0.21	0.78 ± 0.08	3.46 ± 0.20
150 ºC	5.36 ± 0.23	1.02 ± 0.11	0.41 ± 0.07	3.59 ± 0.11
100 ºC	4.09 ± 0.38	0.82 ± 0.07	0.43 ± 0.06	3.55 ± 0.11
25 ºC	3.17 ± 0.24	0.63 ± 0.08	0.30 ± 0.08	3.50 ± 0.12

Table 3. The ratio of etch depths for polyimide, and 3.5 wt % and 7.0 wt % Si_8O_{11} POSS-polyimides to Kapton H$^®$ after exposure to a hyperthermal O-atom beam at five temperatures.

Temperature of the Sample	Polyimide/ Kapton H$^®$ (µm)	3.5 wt % Si_8O_{11} POSS-polyimide/ Kapton H$^®$ (µm)	7.0 wt % Si_8O_{11} POSS-polyimide/ Kapton H$^®$ (µm)
300 ºC	3.30 ± 0.20	0.40 ± 0.06	0.21 ± 0.05
220 ºC	2.16 ± 0.16	0.27 ± 0.06	0.23 ± 0.03
150 ºC	1.49 ± 0.08	0.28 ± 0.03	0.11 ± 0.02
100 ºC	1.15 ± 0.11	0.23 ± 0.02	0.12 ± 0.02
25 ºC	0.91 ± 0.08	0.18 ± 0.02	0.086 ± 0.02

The results show that although POSS-PIs have increased erosion with temperature, they do erode less than their no-POSS analogues at elevated temperatures. In most cases, except at 220 ºC, a doubling of the POSS content from 3.5 wt % to 7.0 wt % Si_8O_{11}, causes the etch depth to decrease by about half. The O-atom fluences used in this study are about half of those used in other work with these materials. It has been seen that at

higher O-atom fluences, at room temperature, there is an increasing difference in the erosion of polyimide and POSS-PI. This is because the erosion of polyimide increases linearly with fluence while the erosion of POSS-polyimide decreases exponentially with fluence.[23] Hence, it is expected that the higher fluence exposures, at elevated temperatures, may reveal a more marked reduction in erosion yields for the POSS-polyimides compared to the erosion yields for the polyimide and Kapton H[®] films.

The physical properties of POSS-PIs were evaluated by DMTA at Edwards Air Force Research Laboratory and have been discussed previously.[15] The glass transition temperatures (Tg) were as follows: 420 ºC for 0 % POSS-PI, 394 ºC for 3.5 % Si_8O_{11} MC-POSS-PI, 390 ºC for 7 % Si_8O_{11} MC-POSS-PI, 383 ºC for 8.75 % Si_8O_{11} MC-POSS-PI. The 7 % Si_8O_{11} MC-POSS-PI exhibited a tan δ peak very similar in intensity and breadth to the 0 % POSS-I peak, while the 3.5 and 8.75 wt % Si_8O_{11} MC-POSS-PI tan δ peaks were slightly greater than half the height, and of similar width, to the 0 and 7 wt % POSS samples.[18] This unique behavior of the 7 wt % Si_8O_{11} MC-POSS-PI may be from similar chain packing to the 0 % POSS-PI sample. A side-chain POSS (SC-POSS) monomer has been synthesized by Wright et al. [19] and was readily copolymerized to form POSS-PIs with POSS as a pendant group. In an AO exposure with a total fluence of 3.53 x 10^{20} O atoms cm^{-2}, 7 % Si_8O_{12} SC-POSS-PI had an erosion yield that was 3.3 % of Kapton H[®]. In a previous AO exposure study total fluence of 4.10 x 10^{20} O atoms cm^{-2}, 7 % Si_8O_{11} MC-POSS-PI had an erosion yield that was 3.8 % of Kapton H[®]. These results indicate that MC- and SC-POSS-PIs have approximately equal AO resistance. DMTA measurements taken at Michigan State University (consistently 20 ºC less than those taken at Edwards AFB due to instrumentation) have shown that the Tg of 7 wt % Si_8O_{12} SC-POSS-PI is 400 ºC, and decreases to 378 ºC after exposure to 2.3 x 10^{20} O atoms cm^{-2}. The tan δ peaks for this material were slightly more intense and broader than commercial Kapton H[®].

The sudden temperature changes experienced by materials in the LEO environment make the coefficient of thermal expansion (CTE) an important material property. The CTE values for several samples are shown in Table 4. The addition of POSS slightly increases the CTE, and a slight decrease is seen after exposure of the SC-POSS-PI to AO. Mismatches in the CTEs between polymeric materials and their coatings lead to cracks, crazing, and mechanical material failure. The CTE of fused silica is about 0.55 (μm/m°C) [27, 28] and the CTE of the silica passivation layer formed on POSS-PIs in the presence of AO is expected be close to that of silica in value. This mismatch between the silica passivation layer and the underlying POSS-PI is likely to cause cracks in the silica. The self-passivating properties of the POSS-PIs described above result in the formation of a silica passivation layer in the areas where cracks or damage have occurred, once again protecting the underlying POSS-PI.

Table 4. Coefficients of Thermal Expansion for POSS polyimide films.

Sample	*CTE (μm/m°C)*
Kapton H[®]	30.25
0 % POSS-PI	33.11
7 % Si_8O_{11} MC-POSS-PI	33.5
8.75 % Si_8O_{11} MC-POSS-PI	35
7 % Si_8O_{12} SC-POSS-PI	35.86
7 % Si_8O_{12} SC-POSS-PI exposed to AO[†]	33.64

*Test variability based on 5 Kapton H[®] tests = ± 2.306 ppm / °C.
[†]2.3×10^{20} oxygen atoms cm^{-2}

MC-POSS-PI films were flown on the Materials International Space Station Experiment (MISSE-1). The flight was launched on August 10, 2001 and was retrieved after 3.9 years in LEO. The sample holder was exposed to all aspects of the LEO environment with the predominant species being AO and UV light. Various images of the samples were taken throughout the flight which show that the 0 % POSS-polyimide was completely eroded by Dec. 05, 2001, while the POSS-polyimide films remained. This demonstrates that the 0 % POSS-PI samples survived in LEO for less than four months. Images of the samples during the first four months of flight are not available, so the erosion rate of the 0 % POSS-PI sample is not known for this experiment.

The POSS-polyimides included a 0, 1.75, and 3.5 wt % Si_8O_{11} MC-POSS-PIs and the flown materials are shown in Figure 3. The samples are shown on the aluminum disc substrates on which they were flown. The outer ring of the films was protected from exposure to the space environment.

The innermost portions of the samples were thinner than the portion closer to the unexposed (masked) area. This inner area may have eroded more, or may have been thinner before flight, or both scenarios may have occurred. The film thicknesses and uniformity were not characterized prior to flight. The step heights from the unexposed area and the neighboring exposed portion of the sample were measured in 12 places around the circumference of the exposed sample area. From these twelve step-height measurements, it was determined that the thickness of the masked 0 % POSS-polyimide is 32.55 ± 0.87 μm, with the exposed portion completely eroded, revealing the aluminum substrate. This substrate has multiple indents and scratches, presumably due to micrometeroid debris impacts. 1.75 % MC-POSS-PI showed some survival with a step height of 5.79 ± 1.31 μm between the exposed outermost portion and the masked area, although the inner portion of this sample completely eroded. 3.5 % MC-POSS-PI film remained throughout with a step height of 2.12 ± 0.34 μm from the outermost portion and the unexposed area, and an inner region with decreased thickness. Ground-based AO exposures have shown even erosion of POSS-polyimides, indicating that the uneven

erosion may be due to initially non-uniform samples. It was determined by XPS that the atomic percentages of the top 10 nm of the films were 34 % Si, 59 % O, and 7 % C for both the 1.75 and 3.5 wt% Si_8O_{11} MC-POSS-PI samples. Therefore the resultant passivation layer is of the same composition for both POSS concentrations. A more detailed inspection of these samples will be published.

Figure 4 shows a microscopic image of (a) 1.75 wt % Si_8O_{11} MC-POSS-PIs that was impacted by micrometeroid. This image shows the tear through the POSS-polyimide film material and the damage to the underlying aluminium substrate. Micrometeoroids can mimic a sandblasting effect on materials. When silica-coated-Kapton is impacted by a micrometeroid, the underlying Kapton is exposed along the edges of the tear, and erodes. POSS-Kapton maintains the ability to form a silica layer in all scratched or torn areas, resulting in decreased material erosion. Figure 4 (b) shows scratches on the surface of 3.5 wt % Si_8O_{11} MC-POSS-PIs and image (c) is of one of the thinnest areas of the 3.5 wt % Si_8O_{11} MC-POSS-PI samples. These areas appear as completely eroded in the image shown in Figure 3, although a very thin layer of material is witnessed throughout the sample by the naked eye. The pattern of scratches on the material surface is similar to samples flown on MISSE-1 by other laboratories.
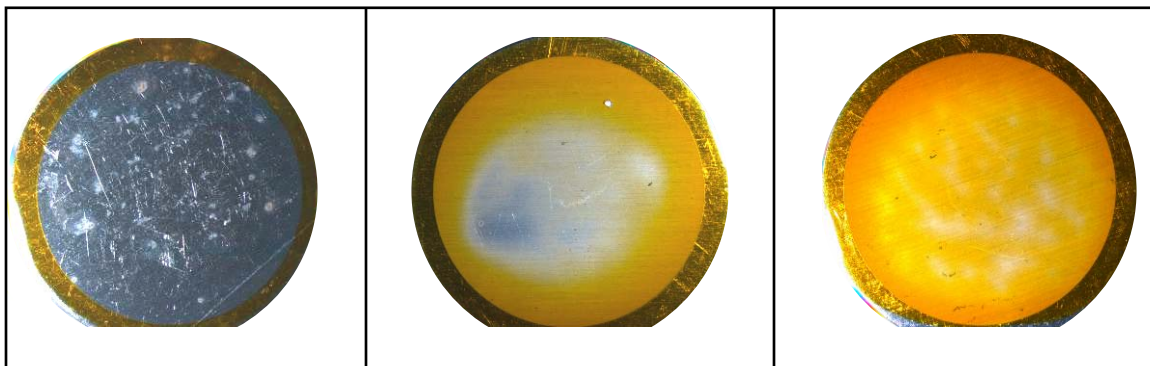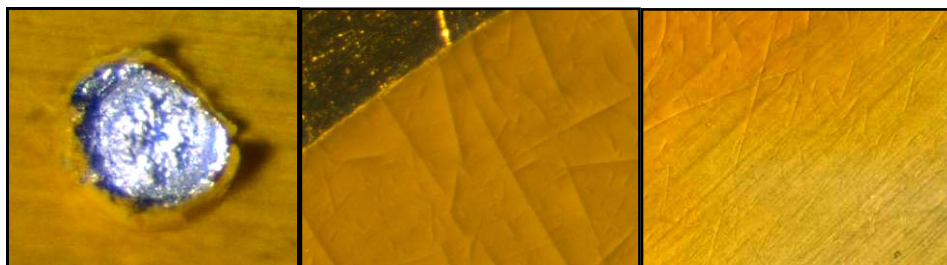

Figure 3. From left to right, 0, 1.75, and 3.5 wt % Si_8O_{11} MC-POSS-PIs flown for 3.9 years in LEO on MISSE1. The outer ring of material was not exposed to the space environment.

Figure 4.   15X magnification of (a) 1.75 wt % Si_8O_{11} MC-POSS-PIs that has been impacted by micrometeoroid debri, (b) 3.5 wt % Si_8O_{11} MC-POSS-PI in the masked (upper left) and exposed neighboring area, (c) 3.5 wt % Si_8O_{11} MC-POSS-PI in one of the thinnest inner areas.

4. CONCLUSION

The incorporation of POSS nanostructures into polyimides has been shown to significantly extend the lifetime of these materials in LEO. Studies on the effect of a hyperthermal O-atom beam on POSS-PIs have shown the improved oxidation resistance imparted to polyimides by the addition of POSS. XPS data of both the AO-exposed and space-flown POSS-PI materials indicated that the improved oxidation resistance of these materials is due to a silica layer that is formed upon exposure of POSS-PIs to high incident fluxes of atomic oxygen.

A study of the response of scratched materials to AO showed that if a Kapton H[®] surface is scratched, the scratched material will erode at roughly the same rate as undamaged Kapton H[®]. A SiO_2 coating of 130 nm protected underlying polyimide from AO attack, but after the coating was compromised, the exposed polymer eroded (during AO exposure) at approximately the same rate that uncoated Kapton[®] eroded. The 8.75 wt % Si_8O_{11} MC-POSS-PI experienced roughly 1 - 2 % the erosion yield of Kapton H[®] that was exposed to an equivalent amount of AO. This difference can be accounted for by the formation of a silica layer on the surface of the material during AO exposure. When this layer was removed by a scratch, newly AO-exposed material had the same low erosion yield, indicating that a silica passivating layer formed in the scratched area.

It was found that the incorporation of POSS slightly reduces the glass transition temperature (Tg) of Kapton[®] polyimide, however, the Tg values of POSS-PIs are well above the temperatures experienced by materials in LEO. The CTE of POSS-PIs is similar to the CTE of commercial Kapton H[®]. A new SC-POSS monomer imparts about the same AO resistance to polyimides as the MC-POSS monomer. The modulus, Tg, and CTE of SC-POSS-PIs were determined before and after exposure to atomic oxygen, and are comparable to the values of these properties for Kapton H[®].

Polyimide and POSS-PI samples flew in LEO on the International Space Station for 3.9 years. The samples were exposed to both AO and UV light. The polyimide sample completely eroded before 4 months, and a thin film of the 3.5 wt % Si_8O_{11} POSS-polyimide remained after the flight demonstrating the space-survivability of POSS-PIs.

5. ACKNOWLEDGMENTS

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